(C(1')), 39.3 (C(2')), 72.0 (C(3')), 69.3 (C(4')), 72.5 (C(5')), 62.2 (C(6')).

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Simple catalytic synthesis of 3,3,5-trimethylcyclohexylamine

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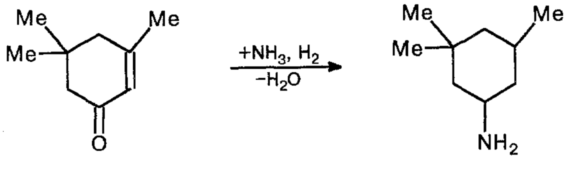
Catalytic inter- and intramolecular hydroamination of aldehydes and ketones occupy a prominent place among the practical methods for preparing amines.[1] A process in which the $>C=O$ and $>C=C<$ groups incorporated in the molecule of a starting carbonyl compound are simultaneously converted into $>CH-NH_2$ and $>CH-CH<$ groups, respectively, under conditions of hydroamination is of interest from the synthetic viewpoint. In this case, the products of crotone condensation of aldehydes and/or ketones are convenient synthons for the synthesis of amines. We found that in the presence of the copper—zinc—aluminum-containing SNM-1 catalyst, which is used in the industrial synthesis of methanol and is capable of accelerating amination,[2] isophorone (**1**) reacts with hydrogen and ammonia to give 3,3,5-trimethylcyclohexylamine (**2**):



1 **2**

Vapor-phase hydroamination of **1** was carried out in a flow-type reactor with a fixed bed of SNM-1 (30 cm^3). The products were analyzed by GLC (Chrom-5) and identified on a Kratos-MS-25RF/DS-90 GC-mass spectrometer. The reaction of **1** with a hydrogen—ammonia mixture was carried out at a temperature of 210—220 °C, a total pressure of 3.5 MPa, an $H_2 : NH_3$: **1** molar ratio of 1 : 0.75 : (0.02—0.03), and a specific rate of introduction of **1** of 2.2 mol $(h\ L\ Cat)^{-1}$. Under these conditions, the degree of conversion of **1** was more than 99 % (w/w). The major product of the conversion of **1** was 3,3,5-trimethylcyclohexylamine **2**, whose yield was 90—95 % (w/w). Along with amine **2**, 4—6 % (w/w) di(3,3,5-trimethylcyclohexyl)amine (**3**) and 1—3 % (w/w) 1,1,3-trimethylcyclohexane (**4**) were obtained. Secondary amine **3** results apparently from hydrogenation of the Schiff's base formed in the condensation of **1** with **2**, and **4** results from the exhaustive hydrogenation of **1**.

MS, *m/z* (I_{rel} (%)), compound **2**: 141 $[M]^+$ (11), 116 (16), 114 (7), 109 (18), 85 (9), 84 (92), 83 (20), 82 (7), 71 (12), 70 (100), 69 (13), 68 (11), 67 (10), 57 (16), 56 (20), 52 (27), 53 (7), 44 (38), 43 (76), 42 (24), 41 (50), 40 (6), 39 (23); **3**: 265 $[M]^+$ (4), 250 (9), 209 (7), 208 (40), 195 (7), 194 (42), 89 (7), 70 (22), 69 (19), 57 (8), 55 (20), 45 (48), 44 (100), 43 (27), 42 (7), 41 (27), 39 (7); **4**: 126 $[M]^+$ (2), 112 (10), 111 (100), 83 (29), 70 (20), 69 (95), 68 (6), 67 (12), 57 (15), 56 (32), 55 (60), 53 (10).

Thus, catalytic hydroamination of compound **1** can serve as the effective preparative-scale method for preparing compound **2**.

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Anomalous radiothermoluminescence at temperatures above the region of decay of primary products of radiolysis

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Radiothermoluminescence (RTL) of frozen solutions normally consists of one or more maxima located at temperatures higher than the temperature of irradiation; each of these maxima coincides with the temperature range of recombination of one or another primary products of radiolysis.[1] Previously it has been assumed that at the temperature at which RTL ceases, recombination processes also stop. Hence, if irradiation is carried out at exactly the temperature of completion of RTL, subsequent heating should not lead to any luminescence, since all of the primary radiolysis species have characteristic intervals of existence, located at lower temperatures.

We found anomalous behavior of tetramethylene sulfoxide (TMSO). When it is irradiated at 77 K, the RTL is completed already at 180 K (Fig. 1, *a*). However, irradiation of TMSO at an even higher temperature (194.5 K, solid CO_2), to which the primary products of radiolysis should not have survived (Fig. 1, *b*), unexpectedly gave a new RTL curve recorded during heating.

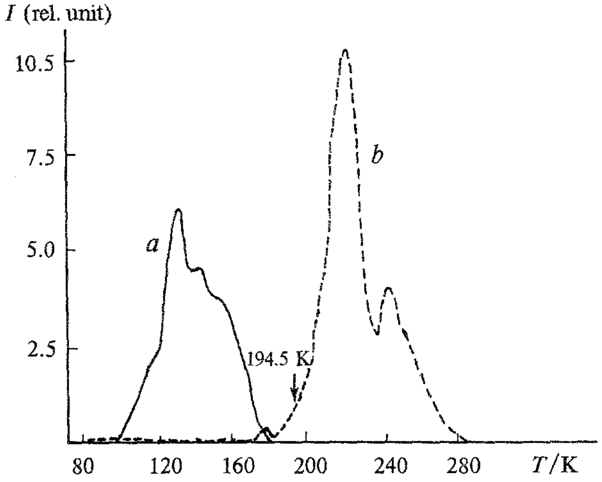

Fig. 1. Radiothermoluminescence of TMSO after γ-irradiation (with a dose of 10^4 Gy) at 77 K (*a*) and 194.5 K (*b*) (after irradiation, the specimen was cooled to 77 K).

Previously[2] we reported that $SO_4^{\cdot -}$ radical ions may be stabilized in solutions of sulfuric acid at 194.5 K (the temperature of irradiation) or at higher temperatures. These radicals, generated by irradiation at 77 K, normally decay even below 180 K. Their anomalous stability was explained by the conditions of cooling that ensured the formation of a particular phase composition during freezing of the solution of sulfuric acid. Another possible reason is anomalous stability of the products of radiolysis of TMSO at temperatures above 194.5 K. However, it may also be significant that irradiation temperature can accidentally fall within an interval between phase transitions in a frozen solution of TMSO, when the rates of chemical transformations dramatically decrease and this would enable accumulation of unstable primary products. While studying low-temperature chemiluminescence of the reaction of XeF_2 with uranium(IV) in solutions of sulfuric acid, we observed several luminescence maxima. Although the reaction itself remained the same, its rate increased at temperatures of phase and relaxation transitions and dramatically decreased in the intervals between them.[3] It is this effect, named the "Hadwall effect," that possibly[4] accounts for the anomalous RTL observed.

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